PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-037964
(43)Date of publication of application : 08.02.2000

(51)Int.Cl. B41N 1/08
B41N 3/03

(21)Application number : 10-209845
(22)Date of filing : 24.07.1998

(71)Applicant : FUJI PHOTO FILM CO LTD
(72)Inventor : SAWADA HIROKAZU
SAKAKI HIROKAZU

(54) LITHOGRAPHIC PRINTING PLATE SUBSTRATE

(57)Abstract:
PROBLEM TO BE SOLVED: To manufacture a lithographic printing plate substrate having superior plate checking properties and surface shape whose surface is roughened uniformly by the electrochemical surface roughening treatment.
SOLUTION: The surface roughening treatment including the electrochemical roughening is applied to a plate material containing Fe: 0.2–0.4 wt.%, Si: 0.03–0.15 wt.%, Cu: 0.006–0.03 wt.% and Ti: 0.020–0.030 wt.% and satisfying Ti/Cu: 1–5, in which the remaining portion is composed of unavoidable impurities and Al, and the Al purity is 99.3 wt.% or more, and the length in the plate width direction vertical to the rolling direction of crystalline particles located on an area up to the 5 μm depth in the thickness direction of the surface of the substrate is 30 μm–150 μm and the length in the direction conforming to the rolling direction is 100–3,000 μm.

LEGAL STATUS

[Date of request for examination]	24.02.2004
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	
[Date of registration]	
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] Fe: 0.2 - 0.4wt% and Si:0.03 - 0.15wt% and Cu:0.006 - 0.03wt%, Contain Ti:0.020 - 0.030wt% and Ti/Cu:1-5 are filled. Board width lay length vertical to the rolling direction of the crystal grain which aluminum purity is more than 99.3wt%, and is located in the field from the front face to a thickness direction depth of 5 micrometers by the remainder consisting of an unescapable impurity and aluminum by 30 micrometers - 150 micrometers And the base material for the lithography versions characterized by coming to give split-face-ized processing which includes electrochemical split-face-ization for the front face of a plate whose lay length which is in agreement with a rolling direction is 100 micrometers - 3000 micrometers.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] About the base material for the lithography versions, especially this invention has a uniform split-face-ized configuration by electrochemical split-face-ized processing, and it is related with the base material for the lithography versions which was excellent ****** and in the shape of a field.
[0002]
[Description of the Prior Art] Conventionally, the aluminium alloy plate is used as a base material for the lithography versions. And split-face-ized processing is performed in order that this aluminium alloy plate may give adhesion with a sensitization layer, and the water retention of the non-image section. It is the electrochemical split-face-ized method and acid solution which carry out electrolytic polishing of the front face of an aluminium alloy plate from the former as the split-face-ized approach using the electrolytic solution which makes a subject mechanical split-face-ized methods, such as a ball grain and a brush grain, a hydrochloric acid, a nitric acid, etc. Although the chemical split-face-ized method which etches the front face of an aluminium alloy plate is learned, in recent years, the split face acquired by the electrochemical split-face-ized method has a homogeneous pit (irregularity), and since it excels in the printing engine performance, it is becoming in use to split-face-ize combining this electrochemical split-face-ized method and other split-face-ized approaches.
[0003] However, also in this electrochemical split-face-ized processing,-like [, such as unevenness of the shape of a muscle called the nonuniformity of the shape of rough skin called surface condition ZARATSUKI depending on the aluminium alloy plate to be used and a streak, / field / poor] has arisen. It is known that-like [field / such poor] originates in the crystalline structure of the surface part (field with a depth [a front face to] of about several micrometers) of an aluminium alloy plate, and many things are examined about the crystalline structure, especially the magnitude and the configuration of a crystal with the aluminium alloy presentation. For example, the base material for the lithography versions which contained Ti:0.005 - 0.020wt% Cu:0.0054 - 0.04wt% Si:0.03 - 0.1wt% Fe:0.25 - 0.5wt%, and split-face-ized electrochemically the aluminium alloy plate whose magnitude of a direction perpendicular to the rolling direction of the macrostructure grain of the outermost surface layer is 50-200 micrometers is indicated by JP,8-179496,A. moreover -- JP,63-47349,A -- Mg:0.30 - 1.0wt% and Si:0.3 - 1.3wt% and Cu:0.003 - 0.10wt% -- it contains and the aluminium alloy plate whose average width of face of the crystal grain of the direction of the board width perpendicular to a surface rolling direction is 40 micrometers or less is indicated.
[0004]
[Problem(s) to be Solved by the Invention] However, although, as for the conventional aluminium alloy plate which was mentioned above, effectiveness is accepted in an improvement of a streak, the improvement of surface condition ZARATSUKI has the problem that it is not enough and is inferior to the homogeneity of the formation of an electrochemical split face. Furthermore, in production of the usual lithography version, although there is the no ** version activity at the time of the ability of an image to be burned, i.e., lack of an image, or although checking by

viewing whether the image remains in the unnecessary part is performed, if the front face of a base material is blackish in that case, visibility will fall and it will come to have a bad influence on the accuracy of the ** version activity. With the conventional aluminium alloy plate, since there are few contents of Ti, when it considers as a base material, a front face tends to become black, and it has become hindrance when doing the exact ** version activity.
[0005] This invention is made in view of such a situation, and split-face-izing by electrochemical split-face-ized processing is uniform, and it aims at offering the base material for the lithography versions which was excellent ****** and in the shape of a field.
[0006]
[Means for Solving the Problem] As a result of repeating research wholeheartedly that the above-mentioned technical problem should be solved, by specifying the magnitude of the crystal grain which considers an aluminium alloy plate as a specific alloy presentation, and is located in the surface section, this invention persons find out uniform split-face-ization exceeding the former and that an improvement of the shape of ****** and a field can be realized, and came to complete this invention. The above-mentioned purpose Namely, this invention [Fe:0.2 - 0.4wt% of], and Si:0.03 - 0.15wt%, Ti:0.020 - 0.030wt% is contained Cu:0.006 - 0.03wt%. And fill Ti/Cu:1-5 and the remainder consists of an unescapable impurity and aluminum. Board width lay length perpendicular to the rolling direction of the crystal grain which aluminum purity is more than 99.3wt%, and is located in the field from the front face to a thickness direction depth of 5 micrometers by 30 micrometers - 150 micrometers And the lay length which is in agreement with a rolling direction is attained by the base material for the lithography versions characterized by coming to give split-face-ized processing which includes electrochemical split-face-ization for the front face of the plate which is 100 micrometers - 3000 micrometers.
[0007]
[Embodiment of the Invention] Hereafter, this invention is explained to a detail. As for Fe, 0.2 - 0.4wt% is added in the base material for the lithography versions of this invention. It lifting-comes to be easy of a version piece, in case a mechanical strength passes low over it and a content attaches it in the printing cylinder of a printing machine as a lithography version less than [0.2wt%], since Fe affects the reinforcement of a base material greatly. On the other hand, since fitness nature comes to be inferior and it lifting-comes to be easy of a version piece during printing in case it will become the high intensity beyond the need and will attach in the printing cylinder of a printing machine as a lithography version, if a content exceeds 0.4wt(s)%, it is not desirable. The case of the printing version used for a proof application becomes however, less important for the constraint about these fitness nature or reinforcement.
[0008] Since Si is contained as an unescapable impurity in aluminum metal which is a raw material, in order that it may prevent the variation by the raw-material difference, minute amount addition of it is carried out intentionally in many cases. When the content exceeded 0.15wt(s)% and it prints at that time, there is fault that the non-image section dirt-comes to be easy. On the other hand, since it may already have a content beyond 0.03wt% depending on a raw material, the numeric value below this is not realistic. Moreover, Si has the effectiveness which forms aluminum-Fe-Si system metallic compounds, and equalizes an electrolysis split face, therefore, less than [0.03wt%], this effectiveness is not acquired for a content. Furthermore, since a high grade aluminum metal expensive in order to maintain less than [0.03wt%] as a content is needed, it is not realistic from this point. therefore, the content of Si -- 0.03 - 0.15wt% -- it may be 0.04 - 0.10wt% preferably.
[0009] Cu is an element very important when controlling electrochemical split-face-ization. Therefore, since, a uniform pit is not formed. [resisting / of the scaling coat at the time of forming a pit electrochemically / a content] [too little / less than / 0.006wt%] On the other hand, if a content exceeds 0.03wt(s)%, since resistance of the scaling coat at the time of forming a pit conversely will become excessive, a big and rough pit becomes is easy to be generated. The uniformity of this pit generation is an indispensable item in order to acquire the outstanding printability. therefore, the content of Cu -- 0.006 - 0.03wt% -- it may be 0.01 - 0.02wt% preferably.
[0010] It is added in order to make detailed conventionally the crystalline structure at the time

of casting, and Ti is an element, and is the form of an aluminum-Ti alloy, or is added in the form of an aluminum-B-Ti alloy. However, it is characterized by having found out that Ti participates in equalization of the formation of ** electrochemical split face greatly in this invention, having the effectiveness which disagrees with the above-mentioned property which **Cu has, and that the hue of the base material after split-face-ized processing changed with **Ti contents, and finding out the optimum value of a relative amount with Cu with absolute magnitude. namely, Ti content in this invention -- absolute magnitude -- 0.020 - 0.030wt% -- it is 0.022 - 0.028wt% preferably, and a Ti/Cu ratio is four or less [1.2 or more] preferably five or less [1 or more]. Since resistance of the scaling coat at the time of forming a pit in electrochemical split-face-ized processing becomes [too little] when Ti addition exceeds 0.030wt(s)%, the fault that a uniform pit is no longer formed arises. On the other hand, less than [0.020wt%], the front face of a base material becomes black and an addition comes to cause trouble to the ** version activity. In addition, since cast structure is not made detailed, even after making the thickness of 0.1-0.5mm through various processes, there is fault of producing a defect with the trace of big and rough cast structure remarkable in ****** and an appearance. Moreover, on the occasion of the formation of an electrochemical split face, Ti lowers resistance of a scaling coat, when forming a pit, and on the other hand, Cu is balancing each effectiveness of raising resistance of a surface acid coat and of conflicting, and can realize uniform electrochemical split-face-ization. Therefore, when a Ti/Cu ratio exceeds less than 1 and 5, the homogeneity of a pit all worsens. Moreover, when a Ti/Cu ratio is less than one, it is equivalent to there being few above-mentioned Ti contents, and ****** is worsened.

[0011] Although the remainders of an aluminium alloy are an unescapable impurity and aluminum, the aluminum purity of an aluminium alloy becomes more than 99.3wt% from the maximum total quantity of each component mentioned above.

[0012] The following approach is employable in order to make the above-mentioned aluminium alloy into a plate. First, according to a conventional method, defecation processing is performed and the aluminium alloy molten metal adjusted to the predetermined alloy content is cast. The filter which uses the so-called rigid media filters, such as degasifying processing using flux processing, Ar gas, Cl gas, etc., and a ceramic-tube filter, a ceramic form filter, an alumina flake, alumina balls, etc. as a filtering medium in order to remove unnecessary gas, such as hydrogen in a molten metal, in defecation processing, and filtering using a grass cloth filter etc. Or processing which combined degasifying and filtering is performed.

[0013] Subsequently, the above-mentioned molten metal is cast. About the casting approach, there are an approach using fixed mold represented by the direct chill casting process and an approach using drive mold represented by the continuous casting process, and any approach is possible. For example, when DC casting is performed, the ingot of 300-800mm of board thickness can be manufactured. the ingot -- a conventional method -- following -- facing -- a surface -- 1-10mm is cut desirably 1-30mm. Then, soak-ized processing is performed if needed. When performing soak-ized processing, heat treatment of 1 hours or more and 48 hours or less is performed at 450-620 degrees C so that an intermetallic compound may not make it big and rough. When shorter than 1 hour, the effectiveness of soak-ized processing becomes inadequate. Subsequently, hot rolling and cold rolling are performed and it considers as an aluminum rolled plate. As initiation temperature of hot rolling, it considers as the range of 350-500 degrees C. Intermediate-annealing processing may be performed to the middle a front or the back. [cold rolling] The heat-treatment for 120 or less seconds can be desirably used for the intermediate-annealing conditions in this case at 450-550 degrees C 360 or less seconds by 400-600 degrees C using the approach of heating at 350-500 degrees C desirably by 280 degrees C - 600 degrees C for 2 to 10 hours for 2 to 20 hours using a batch type annealing furnace, and a continuous annealing furnace. The crystalline structure can also be made fine if it heats with the programming rate of 10 degrees C/second or more using a continuous annealing furnace.

[0014] The process so far can adjust the magnitude of the crystal grain located in the field from the front face of an aluminium alloy plate to a thickness direction depth of 5 micrometers in the range whose lay length (it is hereafter called die length) which board width lay length (it is hereafter called width of face) perpendicular to the rolling direction is 30 micrometers - 150

micrometers, and is in agreement with a rolling direction is 100 micrometers - 3000 micrometers. In the base material of the lithography version, in order that field-like homogeneity may make the above-mentioned ****** good, it is a more important item than a white thing and an EQC. It depends for the homogeneity of the shape of this field on the magnitude of the crystal grain located in the surface section of an aluminium alloy plate. The width of face of the crystal grain located in the surface section influences a streak, and the die length of crystal grain influences surface condition ZARATSUKI. In this invention, it found out that the shape of a good field was acquired by specifying the width of face of crystal grain to 30 micrometers - 150 micrometers, and specifying die length to 100 micrometers - 3000 micrometers. In the width of face of crystal grain, since a streak occurs and too much crystal detailed-ization is needed by less than 30 micrometers on the other hand when die length exceeds 150 micrometers, it is not realistic. About the length of crystal grain, since surface condition ZARATSUKI arises and it, on the other hand, needs too much crystal detailed-ization by less than 100 micrometers in exceeding 3000 micrometers, it is not realistic. Especially preferably, the width of face of crystal grain is 35 micrometers - 140 micrometers, and die length is 150 micrometers - 2800 micrometers. Moreover, in the lithography version, if 0-3 micrometers of surfaces of an aluminium alloy plate may be made into the surface of a base material by the application, 4-5 micrometers may be made into the surface of a base material from the surface of an aluminium alloy plate. Therefore, it is significant like this invention to specify the magnitude of the crystal grain in a field with a thickness direction depth of 5 micrometers from the front face of an aluminium alloy plate also from the field of versatility.

[0015] The aluminium alloy plate to which the magnitude of crystal grain was adjusted and predetermined thickness, for example, 0.1-0.5mm, was made may improve smoothness by orthodontic appliance, such as a roller leveler and a tension leveler, further like the above. Moreover, in order to process a board width into predetermined width, letting a slitting machine line pass is also usually performed.

[0016] Thus, split-face-ized processing is performed in order to use the made aluminium alloy plate as the base material for the lithography versions subsequently. As mentioned above, it is desirable for the aluminium alloy plate of this invention to fit electrochemical split-face-ized processing, therefore to combine suitably electrochemical split-face-ized processing, and mechanical split-face-ized processing and/or chemical split-face-ized processing as split-face-ized processing. Since electrochemical split-face-ized processing is easy to give detailed irregularity to the front face of an aluminium alloy plate, it is suitable for making the lithography version which was excellent in printing nature. This electrochemical split-face-ized processing is performed in the water solution which makes a nitric acid or a hydrochloric acid a subject using a direct current or an alternating current. The pit of the shape of a crater with an average diameter of about 0.5-20 micrometers or a honeycomb is generable at 30 - 100% of rate of area on an aluminum front face with this split-face-ization. The pit prepared here has the operation which improves the dirt hard and print durability of the non-image section of the printing version. In this invention, especially the terms and conditions of this electrochemical split-face-ized processing are not limited, and can be performed on general conditions.

[0017] Mechanical split-face-ized processing combined with this is performed in order to make an aluminium alloy plate front face into 0.35-1.0 micrometers of average surface roughness generally. In this invention, especially the terms and conditions of this mechanical split-face-ized processing can be performed according to the approach indicated by JP,6-135175,A and JP,50-40047,B, for example, although not restricted. Moreover, especially chemical split-face-ized processing is not restricted, either and a well-known approach can be followed.

[0018] Although anodizing is performed in order to continue at the above-mentioned split-face-ized processing and to usually raise the abrasion resistance of the front face of an aluminium alloy plate, it is desirable to perform anodizing also in this invention. Anythings can be used if a porosity oxide film is formed as an electrolyte used for this anodizing. Generally a sulfuric acid, a phosphoric acid, oxalic acid, chromic acids, or those mixed liquor are used. The concentration of those electrolytes is suitably decided according to an electrolytic class. Since the processing conditions of anodic oxidation change with the electrolyte to be used, it cannot generally specify,

but generally, 1 - 80wt%, electrolytic concentration is suitable for it, if solution temperature is in 5-70 degrees C, current density 1 - 60 A/dm2, electrical potential differences 1-100V, and the range for 10 seconds - electrolysis time amount 300 seconds.
[0019] Moreover, in order to improve the dirt engine performance at the time of printing, it may rinse, after it rinses after performing electrochemical split-face-ized processing and rinsing and an alkali solution performs slight etching processing, and H2SO4 solution performs De Dis Matt, and direct-current electrolysis may be succeedingly performed in H2SO4 solution, and an anodic oxide film may be prepared. Furthermore, hydrophilization processing by silicate etc. may be performed if needed.
[0020] Although the base material for the lithography versions of this invention is obtained as mentioned above, when the pit is formed in homogeneity, and does not have-like [, such as a streak and surface condition ZARATSUKI, / field / poor] and this base material is used as the lithography version, good image quality is acquired. Moreover, the front face is also presenting the hue near white or gray, and the ** version activity can be done easily. In addition, what is necessary is to apply and dry sensitization material and just to form a sensitization layer in a front face, in order to consider as the lithography version. Especially sensitization material is not limited and can usually use what is used for the photosensitive lithography version. And it can consider as the printing version which can attach an image in a printing machine by performing baking and a development, and gum length processing using a lith film. Moreover, if a high sensitivity sensitization layer is prepared, an image can also be directly burned using laser.
[0021]
[Example] After carrying out DC casting using the aluminium alloy of the presentation shown in Table 1 and carrying out facing of the ingot, while performing soak-ized processing, hot rolling, intermediate annealing, and cold rolling one by one, processing conditions were changed and the aluminium alloy plate which adjusted the magnitude of the crystal grain located in a field with a depth of 5 micrometers from a front face as shown in Table 2 was produced. After measurement of the magnitude of crystal grain carried out about 1-1.5-micrometer buffing of the front face of an aluminium alloy plate using alumina suspension (particle diameter of 0.05 micrometers), observation of the grain boundary of it was enabled by performing about 0.5-1.0-micrometer etching with HF solution 10%, it took a photograph of the crystalline structure with the polarization microscope, and measured the width of face and die length of crystal grain from the photograph. And the following split-face-ized processings were performed about each aluminium alloy plate. First, brush grain processing was performed supplying PAMISU suspension on the surface of a plate, and mechanical split-face-ized processing was performed. Subsequently, after rinsing the front face, the NaOH solution performed etching processing, after [rinsing] HNO3 solution performed the desmut treatment, and electrochemical split-face-ized processing was further performed by performing alternating current electrolysis in after [rinsing] HNO3 solution. It etched lightly with the thin NaOH solution after rinsing, and after [rinsing] H2SO4 solution performed De Dis Matt. And direct-current electrolysis was performed in the after [rinsing] H2SO4 solution, the anodic oxide film was formed, and the base material of an example and the example of a comparison was produced.
[0022] About each processed base material, the homogeneity of a pit, ****** (whiteness degree), and field-like evaluation were performed like the above. The homogeneity of a pit carried out SEM observation, judged the split face, made the case where size had gathered as "O", and made "x" the case where that was not right. ****** used together and evaluated visual evaluation and a whiteness degree meter, and made the case of "O" and a too blackish color "x" for the case where come out white and contrast with the image section is made clearly. Field-like evaluation investigated the existence of generating of a streak (stripe-like nonuniformity) and surface condition ZARATSUKI (rough skin-like nonuniformity), made the case where it had not generated visually as "O", and made "x" the case where it had generated. Each evaluation result was shown in Table 2.
[0023]
[Table 1]

成分	Si	Fe	Cu	Mn	Mg	Zn	Ti	Al	Ti/Cu
①	0.06	0.30	0.017	0.001	0.001	0.001	0.03	99.6	1.8
②	0.10	0.35	0.015	0.001	0.001	0.001	0.022	99.5	1.5
③	0.15	0.35	0.006	0.001	0.010	0.001	0.03	99.4	5
④	0.04	0.32	0.024	0.001	0.001	0.001	0.015	99.6	0.6

[0024]
[Table 2]

	成分	表層結晶粒のサイズ		電解粗面化の均一性	検版性（白色度）	面状
		幅（μm）	長さ（μm）			
実施例－1	①	140	2800	○	○	○
実施例－2	②	60	600	○	○	○
実施例－3	③	35	150	○	○	○
実施例－4	①	50	500	○	○	○
比較例－1	④	70	800	△	×	○
比較例－2	④	170	3350	△	×	×
比較例－3	①	150	3100	○	○	×

[0025] In the example, it can consider as the base material for the lithography versions which the uniform pit was formed of electrolysis split-face-ization, and was excellent in ******, and was excellent also in the shape of a field by having made magnitude of crystal grain into predetermined within the limits as shown in Table 2. On the other hand, even if the magnitude of crystal grain is within the limits of this invention in the example -1 of a comparison with a Ti/Cu ratio out of range [this invention], a front face is inferior to ****** black, and the homogeneity of a pit is not so good, either. Moreover, both a streak and surface condition ZARATSUKI occur in the example -2 of a comparison with this invention out of range, the width of face and die length of crystal grain have the poor shape of a field, since this invention is out of range, the Ti/Cu ratio of ****** is still worse, and the homogeneity of a pit is not so good, either. Moreover, in the example -3 of a comparison with the die length of crystal grain out of range [this invention], surface condition ZARATSUKI occurs and the shape of a field is made into the defect.
[0026] Although the above example showed the example which combined mechanical split-face-ized processing and electrochemical split-face-ized processing as split-face-ized processing, it cannot be overemphasized that it is applicable to all the base materials for the lithography versions that this invention shows the outstanding electrochemical split-face-ized property, and does not show the shape of outstanding ****** and a field, and is not limited to the above-mentioned example, but perform electrochemical split-face-ized processing.
[0027]
[Effect of the Invention] As explained above, according to this invention, the base material for the lithography versions which electrochemical split-face-ized processing was made by homogeneity and was excellent ****** and in the shape of a field by having specified the magnitude of the crystal grain in the surface section with the alloy presentation is obtained.

[Translation done.]